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Quantifying the role of marine phytoplankton (DMS) in the present day climate system

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3.

THE CONTRIBUTION OF OCEAN-LEAVING DMS TO THE GLOBAL ATMOSPHERIC BURDENS OF DMS, MSA, SO₂ AND NSS SO₄⁻.

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Global Biogeochemical Cycles, 17(4), 1106, 10.1029/2003GB002153 [2003b]

3.1 Abstract

The contribution of ocean-derived DMS to the atmospheric burdens of a variety of sulphur compounds (DMS, MSA, SO₂ and nss SO₄⁻) is quantified from season to season. Such quantification, especially for nss SO₄⁻ (the climate-relevant product of DMS oxidation), is essential for the quantification of the radiative forcing of climate that may be attributable to marine phytoplankton under possible future climate conditions. Three dimensional chemical transport modelling up to the stratosphere is used as a tool in realising this aim. Global datasets on oceanic and terrestrial sulphur sources are used as input. We find that the contribution of ocean-leaving DMS to the global annually averaged column burdens of the modelled compounds is considerable: 11.9 $\mu\text{mol m}^{-2}$ (98% of total global burden) for DMS; 0.95 $\mu\text{mol m}^{-2}$ (94% of total global burden) for MSA; 2.8 $\mu\text{mol m}^{-2}$ (32% of total global burden) for SO₂ and 2.5 $\mu\text{mol m}^{-2}$ (18% of total global burden) for nss SO₄⁻. The mean annual contribution of DMS to the climate-relevant nss SO₄⁻ column burden is greatest in the relatively pristine Southern Hemisphere, where is estimated at 43%. This contribution is only 9% in the Northern Hemisphere, where anthropogenic sulphur sources are overwhelming. The marine algal-derived input of the other modelled sulphur compounds (DMS, MSA and SO₂) is also greatest in the Southern Hemisphere where a lower oxidative capacity of the atmosphere, a larger sea-to-air transfer of DMS and a larger emission surface area lead to an elevation of the atmospheric DMS burden.

3.2 Introduction

Marine phytoplankton are thought to play an important role in the Earth's energy balance. Previously, a direct negative forcing of climate (*i.e.* a reduction in the amount of incoming solar radiation absorbed by the ocean system) was believed to be caused by an increase in the amount of solar radiation returned to the atmosphere and space through backscattering by spatially extensive and highly reflective coccolithophore (phytoplankton) blooms in the ocean [*e.g.* Tyrell *et al.*, 1999]. However, Gondwe *et al.* [2001] have recently found this effect to be

marginal and not enough to perturb global climate.

Marine phytoplankton are further expected to make a contribution to the total radiation reflected by the Earth through indirectly adding to the atmospheric sulphate aerosol burden. Some prominent phytoplankton groups produce dimethylsulphoniopropionate (DMSP), presumably for the purpose of controlling osmotic pressure and relieving photosynthetic and oxidative stress [Kirst, 1996; Stefels, 2000, Kiene *et al.*, 2000, Sunda *et al.*, 2002]. DMSP is released into the water when microalgal cells are ruptured during consumption by zooplankton, after cell lysis at the end of a bloom or

due to viral lysis [Dacey and Wakeham, 1986; Malin *et al.*, 1992; Malin and Kirst, 1997]. Dimethylsulphide (DMS or CH_3SCH_3) is formed as an algal or bacterial enzyme-mediated degradation product of DMSP [e.g. Bates *et al.*, 1994; Stefels, 2000; Kiene *et al.*, 2000]. Most of this DMS is subsequently consumed by bacteria or is photooxidised in the water at a rate depending on microbial activity and photochemical conditions [Kiene *et al.*, 2000], however, the remaining part, which forms only a small fraction of the entire in-water pool of DMS [Kiene and Bates, 1990]), is emitted to the atmosphere where it undergoes chemical transformation to eventually form non sea salt (nss) sulphate aerosols (SO_4^-) and other sulphur products [Charlson *et al.*, 1987; Lin and Chameides, 1993]. Sulphate aerosols play an important role in the earth-atmosphere radiation balance through partial scattering, absorption and reflection of solar and terrestrial radiation. They may also serve as nucleation sites for the formation of cloud droplets which, in turn, play an important role in the Earth's climate through partial scattering, reflection and absorption of solar and terrestrial radiation.

Under a possible warm future climate, it has been hypothesised that algal blooms may become more abundant and that consequently, DMS production and emissions may increase [Charlson *et al.*, 1987]. An increase in cloud condensation nuclei (as would typically result from additional sulphate aerosols of DMS origin) for a constant liquid water content, would lead to a larger concentration of cloud droplets of smaller radius, which would increase cloud optical depth [Bates *et al.*, 1987; Charlson *et al.*, 1992; Boucher, 1995; Feichter *et al.*, 1997; Roelofs *et al.*, 1998]. A decrease in mean droplet size associated with an increase in cloud droplet concentration is, furthermore, expected to inhibit precipitation development and hence increase cloud lifetime [Feichter *et al.*, 1997; Feichter and Lohmann, 1999]. Such an enhancement of cloud lifetime and the resultant increase in fractional cloud cover would increase both the shortwave and longwave radiative influences of clouds [Albrecht, 1989; Quinn *et al.*, 1995]. Inhibited precipitation development might further alter the amount and vertical distribution of water and heat in the atmosphere and thereby modify the Earth's hydrological cycle [Charlson *et al.*, 1992].

Significant progress has, in the past two decades, been made to estimate the contribution of natural (biogenic (including DMS) plus volcanic)

emissions of a number of sulphur compounds, to the present day global atmospheric sulphur cycle using a variety of methods ranging from monitoring, isotopic analyses to modelling [e.g. Schwartz, 1988; Langner and Rodhe, 1991; Ayers *et al.*, 1991; Bates *et al.*, 1992a; Benkovitz *et al.*, 1994; McArdle and Liss, 1995; McArdle *et al.*, 1998; Prospero *et al.*, 1995; Chin *et al.* 1996, 2000a,b; Chin and Jacob, 1996; Pham *et al.*, 1996; Feichter *et al.*, 1996, 1997; Bates and Quinn, 1997; O'Dowd *et al.*, 1997; Roelofs *et al.*, 1998; Davis *et al.*, 1998; Koch *et al.*, 1999; Chen *et al.*, 2000; Barth *et al.*, 2000; Rasch *et al.*, 2000;].

With regard to monitoring, some ice core and atmospheric measurement studies [e.g. Legrand *et al.*, 1991, 1997; Li *et al.*, 1993a; Berresheim *et al.*, 1990, 1991, 1998; Saltzman *et al.*, 1983, 1985; Ayers *et al.*, 1991; Savoie *et al.*, 1989, 1992, 1993, 1994; Prospero *et al.*, 1991, 1995; Mulvaney *et al.*, 1992] have used the MSA: nss SO_4^- ratio (MSA = methanesulphonate, $\text{CH}_3\text{SO}_3\text{H}$) to estimate the biogenic fraction of SO_4^- over various areas. MSA is formed exclusively from DMS while nss SO_4^- has a variety of sources which include DMS oxidation, volcanic and industrial sulphur emissions and so this ratio provides a rough indication of the relative contributions of biogenic and anthropogenic sources to total sulphate levels. However, since such measurements are localised, they have the deficiency of not being spatially comprehensive. The contribution of oceanic DMS to the total sulphur cycle relative to an anthropogenic source can be expected to differ in different areas of the globe and at different times of the year depending on the location and strength of major anthropogenic sulphur sources and the atmospheric conditions prevailing in different regions and at different times of the year. Thus, while MSA: nss SO_4^- ratio studies provide useful insights on the relative biogenic contribution to the sulphur cycle in specific locations, three-dimensional global studies are more appropriate for providing a globe-wide picture of the spatial variation and distribution of this ratio and can help in excluding the possibility that the significance attached to the relationships proposed by the ratio in one area are not completely different elsewhere or at another time of the year.

Another approach in estimating the relative contributions of continental and marine sources to the global sulphur cycle is the use of sulphur isotopes [McArdle and Liss, 1995; McArdle *et al.*, 1998; Patris *et al.*, 2000]. Different sulphur sources have different sulphur isotopic composition and so the isotopic

signature of marine biogenic sulphate (though currently not yet fully constrained) will be different to that of an anthropogenic source.

With respect to modelling studies, most [e.g. Langner and Rodhe, 1991; Benkovitz *et al.*, 1994; Pham *et al.*, 1996; Feichter *et al.*, 1996; Chin and Jacob, 1996; Koch *et al.*, 1999; Chin *et al.*, 2000a,b; Boucher and Pham, 2002] have focussed on apportioning burdens of DMS and/or MSA and/or SO₂ (sulphur dioxide) and/or SO₄⁼ to either natural (volcanic plus biogenic) or anthropogenic sources. In the current study, we focus on isolating and quantifying the fraction of the atmospheric burdens of all four compounds which can be attributed to oceanic algae alone versus those which can be attributed to all other sources (anthropogenic plus all other natural sources). As long as this individual contribution remains unknown, or hidden within the numbers quantifying the total biogenic fraction, quantifying and judging the significance of the climatic effects induced by marine algae alone remains difficult.

Within these modelling studies, Benkovitz *et al.* [1994] report on sulphate column burdens, but only above the N. Atlantic ocean for selected days in two months. Benkovitz *et al.* [1994], Feichter *et al.* [1996], Chin and Jacob [1996], Kasibhatla *et al.* [1997] and Koch *et al.* [1999] present results on the troposphere only. However, it is now being strongly recognised that the inclusion of the stratosphere in global 3-D chemical transport modelling is desirable, especially if radiatively active tracers such as ozone and water vapour are included [e.g. Steil *et al.*, 1998]. Changes in such tracers feedback on dynamic processes within the troposphere and stratosphere which in turn feedback on the spatial distribution of chemical species within the model. Barth *et al.* [2000] and Rasch *et al.* [2000] omit volcanic and biomass burning sources from their simulations. Since these are significant contributors to the total sulphur cycle, their omission can result in a bias in the simulated percentage contributions from considered sources. Langner and Rodhe [1991] and Feichter *et al.* [1996] consider SO₂ as the sole product of DMS oxidation while Langner and Rodhe [1991] and Benkovitz *et al.* [1994] consider the hydroxyl radical (OH) as the sole oxidant of DMS. Today, MSA is also a known DMS oxidation product and the gaseous nitrate radical (NO₃) is recognised as an additional DMS oxidant. Raes *et al.* [2000] report the relative importance of DMS oxidation to total SO₂ concentrations at selected levels of the troposphere.

Through use of a comprehensive global 3-D chemical transport modelling study for 19 vertically-stacked layers, with 5 layers in the planetary boundary layer (~1000-810 hPa), 9 in the free troposphere (810-120 hPa), and 5 in the stratosphere (120-1 hPa) we build upon the results of the above studies. Oceanic DMS emissions are calculated from a globally-interpolated sea surface DMS database [Kettle *et al.* 1999] and we use the Andres and Kasgnoc [1998] database on volcanic emissions which supercedes that used in most other modelling studies discussed above. We report here on the atmospheric column burdens of DMS, MSA, SO₂ and nss SO₄⁼ resulting from both oceanic and terrestrial sources and those resulting from oceanic DMS emissions alone. Such quantification of the present day global column burdens, especially for nss SO₄⁼, is important for the further quantification of the radiative forcing of climate attributable to aerosols of oceanic algal origin under predicted future meteorological conditions.

3.3 Data and Methodology

We make use of version 3 of the 3-D global Chemical Transport Model (Tracer Model 3; TM3) [Houweling *et al.*, 1998; Dentener *et al.*, 1999, 2002; Sciare *et al.*, 2000b; Jeuken *et al.*, 2001]. The model contains comprehensive sulphur chemistry schemes treating the emission of sulphur species from various source types and the removal of sulphur species through both physical processes (dry and wet deposition) and chemical transformation (photochemical, heterogeneous, gas phase and aqueous phase reactions) [Jeuken *et al.*, 2001]. The distribution of chemical species is controlled by 6-hour mean large-scale dynamics defined by ECMWF (European Centre for Medium Range Weather Forecasts) analyses. Computations are made hourly for the meteorologically representative year of 1993. However, we analyse and present results on monthly averaged fields since our focus is on climatology. The model was spun up by first running it for a couple of months (November and December). Initialisation of 1 November was executed with the October monthly mean values of a 1-year run. Output was collected for the entire year of 1993 from 1 January to 31 December. The input data used in this study are aggregated from their original resolutions to the working resolution of 7.5° x 10° and for 19 vertically stacked layers (up to the stratosphere). It is also

possible to run TM3 at finer resolutions (*e.g.* in Jeuken *et al.*, 1999, 2001; Dentener *et al.*, 1999, 2002; Sciare *et al.*, 2000b).

Both terrestrial and oceanic sources of sulphur have been considered. Anthropogenic sources in continental areas include SO₂ producing industrial activities and biomass burning. TM3 inputs on these have been obtained from the Emission Database for Global Atmospheric Research (EDGAR database) [Olivier and Berdowski, 2001]. Terrestrial biogenic sulphur emissions include those of DMS from plants, soils, wetlands and freshwater lakes. TM3 inputs on these have been based on Spiro *et al.* [1992] (0.9 Tg S yr⁻¹). Oceanic DMS emissions (18 Tg S yr⁻¹) are calculated based on globally-interpolated sea surface DMS concentrations obtained from the Kettle *et al.* [1999] database which is currently held and distributed by the University Corporation for Atmospheric Research (UCAR). For the calculation of these emissions, we make use of surface winds within TM3 and the Liss and Merlivat [1986] air-sea exchange model, which predicts the flux of gases across the air-sea interface as being proportional to the product of the concentration difference across the sea-air interface and the gas transfer velocity. This method is widely used and has previously been well described in literature [*e.g.* Andreae, 1986; Charlson *et al.*, 1987; Bates *et al.*, 1992b, 1994; Malin *et al.*, 1992; Chin *et al.*, 1996; Davison *et al.*, 1996; Gabric *et al.*, 1996, 1998; Frost and Upstill-Goddard, 1999].

Recently, sulphur emissions from fossil fuel burning by international shipping have been found to be a significant contributor to atmospheric SO₂ concentrations over most of the global ocean [Capaldo *et al.*, 1999; Corbett *et al.*, 1999]. We include ship emissions in our analyses and utilise emission data from the EDGAR database. The total anthropogenic SO₂ emission considered from the EDGAR database is 78 Tg S yr⁻¹. SO₂ released from volcanoes (13.4 Tg yr⁻¹) is based upon a 25-year global measurement record which has been compiled into a GEIA (Global Emissions Inventory Activity) database by Andres and Kasgnoc [1998]. Both sporadically and continuously erupting volcanoes are considered in this database. In their database, Andres and Kasgnoc assume that sporadic fluxes last only one day and, therefore, sum up the measured SO₂ fluxes from continuously and sporadically emitting volcanoes to produce a combined flux in mass per day. However, on an annual basis, Andres and Kasgnoc note that sporadically emitting volcanoes account for <1% of

the total summed flux. Furthermore, each volcano has a unique injection altitude. The injection altitude of the volcanoes included in the inventory varies between 321 and 5592m. In our model, the volcanoes are considered as point sources, which means that their emissions are localised and not interpolated over the entire globe.

Figure 1 shows a simplified schematic representation of the DMS oxidation process. In the vertical dimension, DMS loss in TM3 mainly occurs in the boundary layer, followed by the free troposphere (Table 1). The polar stratosphere plays a negligible role in DMS chemistry while DMS chemistry is slightly more important in the tropical stratosphere where large scale convective transport inputs DMS into the stratosphere.

The destruction of DMS occurs in the gas phase and is characterised by its daytime oxidation by OH and its night-time reaction with NO₃ [Atkinson *et al.*, 1984; Kreidenweis *et al.*, 1991; Hynes *et al.*, 1993; Atkinson *et al.*, 1997], with these reactions being most effective in the tropical and subtropical zones (see Table 1). In general, field measurements and laboratory experiments indicate that MSA and SO₂ are the dominant stable products formed from these reactions. TM3 considers two major DMS reaction pathways for the formation of SO₂ and MSA [Hynes *et al.*, 1986, 1993; Atkinson *et al.*, 1992; Koga and Tanaka, 1993]: one where both OH and NO₃ abstract a hydrogen atom from a DMS molecule leading to the formation of several intermediate products and eventually SO₂ as a stable end-product and one where OH is added to the S-atom in DMS to eventually yield 25% MSA and 75% SO₂ [Hynes *et al.*, 1986] as stable end-products. The second reaction pathway is effective under low ambient temperatures [Hynes *et al.*, 1986; Barone *et al.*, 1995; Mauldin *et al.*, 1999; Arsene *et al.*, 2001]. The rate coefficient (cm³ molecules⁻¹ s⁻¹) and its temperature dependence function as used in TM3 for DMS + OH → SO₂ + ... is $9.6 \times 10^{-12} \exp(-234/T)$ following Hynes *et al.* [1986] and Atkinson *et al.* [1992]. That for DMS + OH → 0.75 SO₂ + 0.25 MSA is $k_1 M / (1 + k_2 M)$, where $k_1 = 1.7 \times 10^{-42} \exp(7810./T)$, $k_2 = 5.5 \times 10^{-31} \exp(7460./T)$ and $M = O_2$ (molecules cm⁻³) following Hynes *et al.* [1986]. The rate coefficient and its temperature dependence function for DMS + NO₃ → SO₂ + ... as used in TM3 is $1.9 \times 10^{-13} \exp(520/T)$ following Atkinson *et al.* [1992].

MSA is removed from the atmosphere through wet and/or dry deposition while SO₂ loss

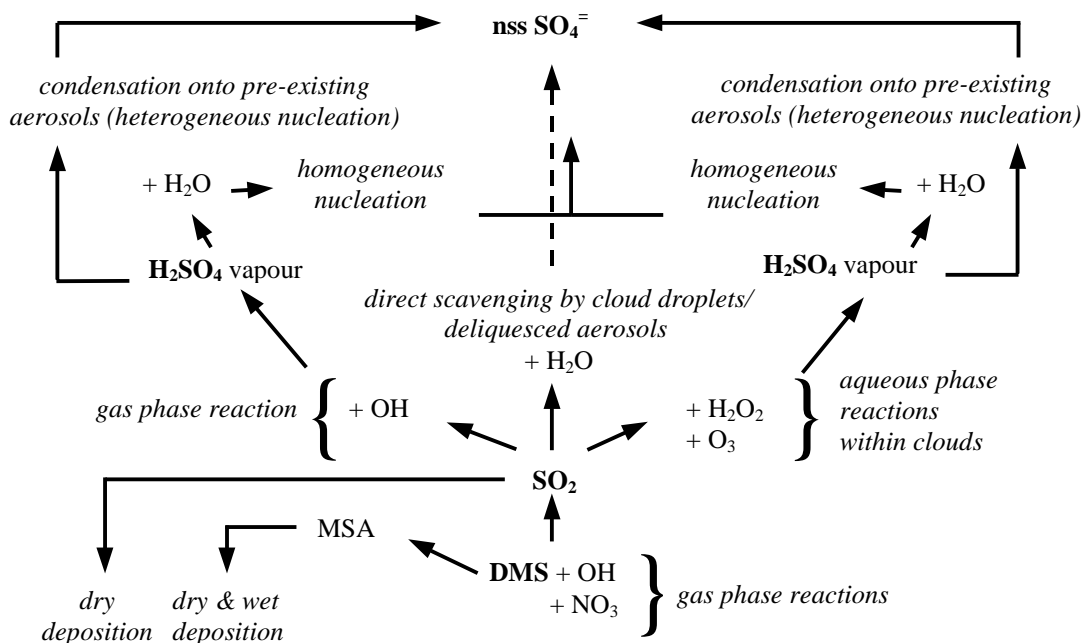


Figure 1: A simplified schematic representation of DMS loss and sulphate aerosol formation processes.

occurs through dry deposition and both gas and aqueous phase reactions. In the gas phase, SO₂ is oxidised by OH to form sulphuric acid (H₂SO₄) while in the aqueous phase (within clouds), it is oxidised by hydrogen peroxide (H₂O₂) and ozone (O₃), when present, also to form H₂SO₄ [Penkett *et al.*, 1979; Ghan *et al.*, 1989; Crutzen and Zimmermann, 1991; Langner and Rodhe, 1991; Lin and Chameides, 1993; Benkovitz *et al.*, 1994; Chin *et al.*, 1996; Lelieveld *et al.*, 1997; Feichter *et al.*, 1997; Roelofs *et al.*, 1998]. The H₂SO₄ formed from SO₂ oxidation undergoes bimolecular homogeneous nucleation with water vapour to form new sulphate aerosols or it condenses onto pre-existing aerosols (heterogeneous nucleation) [e.g. Kreidenweis and Seinfeld, 1988; Jaeger-Voirol and Mirabel, 1989; Kreidenweis *et al.*, 1991; Viisanen *et al.*, 1997]. These physical processes increase the number and size of the sulphate particles, respectively. All chemistry in TM3 is calculated on-line, which means that the oxidant fields (OH, NO₃, H₂O₂ and O₃) contain the variability from both transport and the diurnal cycle. An analysis of the sulphur budget in TM3 and the relative importance of DMS oxidation

pathways in the model atmosphere per geographical region has been made and is presented in Table 1.

TM3 makes use of a technique (referred to as tagged or coloured tracers) to label molecules of DMS originating from an oceanic source and subsequently the molecules of MSA, SO₂, and nss SO₄⁼ produced from it. This has made the model specifically suitable for realising the aim of this study, *i.e.* isolating the fraction of the total atmospheric burdens of DMS, MSA, SO₂ and nss SO₄⁼ that can be attributed to oceanic-algal derived DMS emissions.

Extensive validation of the TM3 model for modelling the relative yields of SO₂ and sulphate in the global atmospheric sulphur cycle, under a setup similar to ours and for the same model year, has previously been made by Jeuken *et al.* [2001] and will not be repeated here. The IPCC [2001] also intercompared several sulphur models, including TM3, and evaluated their performance in reproducing observed sulphate concentrations in the lower atmosphere. Model performance was generally found to be reasonable. However, some shortcomings were noticed in winter when SO₄⁼ was slightly

	Contribution and Relative importance (Megamole S yr ⁻¹)							
	Region							
	90°N - 45°N		45°N - Eq		Eq - 45°S		45°S - 90°S	
DMS Emissions	50933	(100:0:0)	172917	(100:0:0)	238673	(100:0:0)	129937	(100:0:0)
Initial Atmospheric DMS Burden	1484	(33:66+:<1)	760	(61:38+:<1)	978	(85:14+:<1)	1987	(80:19+:<1)
DMS loss by 'DMS + OH → SO ₂ '	-10292	(78:21+:<1)	-65597	(81+18+:<1)	-116736	(78:21+:<1)	-36329	(66:33+:<1)
DMS loss by 'DMS + OH → 25% MSA + 75% SO ₂ '	-16517	(68:31+:<1)	-48923	(62:36:2)	-99599	(63:36:1)	-72014	(57:42+:<1)
DMS loss by 'DMS + NO ₃ → SO ₂ '	-24993	(73:26+:<1)	-63466	(83:16+:<1)	-33821	(69:30+:<1)	-4095	(52:46:2)
Final DMS Burden	1492	(33:66+:<1)	766	(60:39:1)	989	(85:14+:<1)	2042	(80:19+:<1)
Initial MSA Burden	15	(23:51:26)	99	(26:61:13)	294	(46:50:4)	340	(59:40:1)
MSA production from 'DMS + OH → 25% MSA'	4129	(68:31+:<1)	12231	(62:36:2)	24900	(63:36:1)	18004	(57:42+:<1)
MSA loss by Dry Deposition	-534	(100:0:0)	-1341	(100:0:0)	-3167	(100:0:0)	-2687	(100:0:0)
MSA loss by Wet Deposition	-3753	(58:41+:<1)	-11440	(64:34:2)	-21016	(67:32:1)	-15323	(51:48+:<1)
Final MSA Burden	15	(23:50:27)	99	(26:61:13)	296	(46:50:4)	341	(58:40:2)
SO ₂ Emissions	597835	(99+:<1:0)	1742849	(93:7:0)	316533	(76:24:0)	1185	(27:73:0)
Initial SO ₂ Burden	20728	(43:56+:<1)	10748	(67:32:1)	746	(40:50:10)	352	(46:51:3)
SO ₂ Production from 'DMS + OH → SO ₂ '	10292	(78:21+:<1)	65597	(81:18+:<1)	116736	(78:21+:<1)	36329	(66:33+:<1)
SO ₂ Production from 'DMS + OH → 75% SO ₂ '	12388	(68:31+:<1)	36692	(62:36:2)	74699	(63:36:1)	54010	(57:42+:<1)
SO ₂ Production from 'DMS + NO ₃ → SO ₂ '	24993	(73:26+:<1)	63466	(83:16+:<1)	33821	(69:30+:<1)	4095	(52:46:2)
SO ₂ loss by Dry Deposition	-339742	(100:0:0)	-739115	(100:0:0)	-82180	(100:0:0)	-8106	(100:0:0)
SO ₂ loss by Wet Deposition	-125053	(70:29+:<1)	-569473	(77:22+:<1)	-241909	(76:23+:<1)	-53995	(60:39+:<1)
SO ₂ loss by 'SO ₂ + OH → SO ₄ ⁻ '	-40174	(81:18+:<1)	-157161	(77:22:1)	-27850	(60:38:2)	-1705	(41:56:3)
SO ₂ loss by 'SO ₂ + O ₃ → SO ₄ ⁻ '	-9385	(56:44:0)	-56324	(38:62:0)	-45707	(41:59:0)	-5162	(65:35:0)
SO ₂ loss by 'SO ₂ + H ₂ O ₂ → SO ₄ ⁻ '	-102204	(54:46:0)	-419147	(60:40:0)	-141402	(62:38:0)	-25706	(63:37:0)
SO ₂ Final Concentration	20749	(43:56+:<1)	10714	(67:32:1)	746	(40:50:10)	349	(45:52:3)

Table 1: Annual sulphur budget in TM3: Relative importance of DMS oxidation pathways in the model atmosphere per geographical region. The values in brackets are the percentage contribution in the boundary layer (model layers 1-5; ~1000-810 hPa); percentage contribution in the free troposphere (model layers 6-14; 810-120 hPa); percentage contribution in the stratosphere (model layers 15-19; 120-1 hPa). The values presented here are for a closed budget. Overestimation of DMS and SO₂ loss by TM3 is small (0.003% and 0.1%, respectively).

underestimated and SO₂ was overestimated due to shortcomings in the winter SO₂ oxidation processes in the model [Jeuken *et al.* [2001]. Validation of DMS and MSA outputs was not made by Jeuken *et al.* [2001] and so we analyse TM3 results against published marine boundary layer measurements of these species where available (Table 2). Discussion of Table 2 occurs within various appropriate paragraphs

of the following section on “*Results and Discussion*”.

3.4 Results and Discussion

3.4.1. Dimethylsulphide (DMS)

December-January-February, June-July-August and annual mean column burdens of

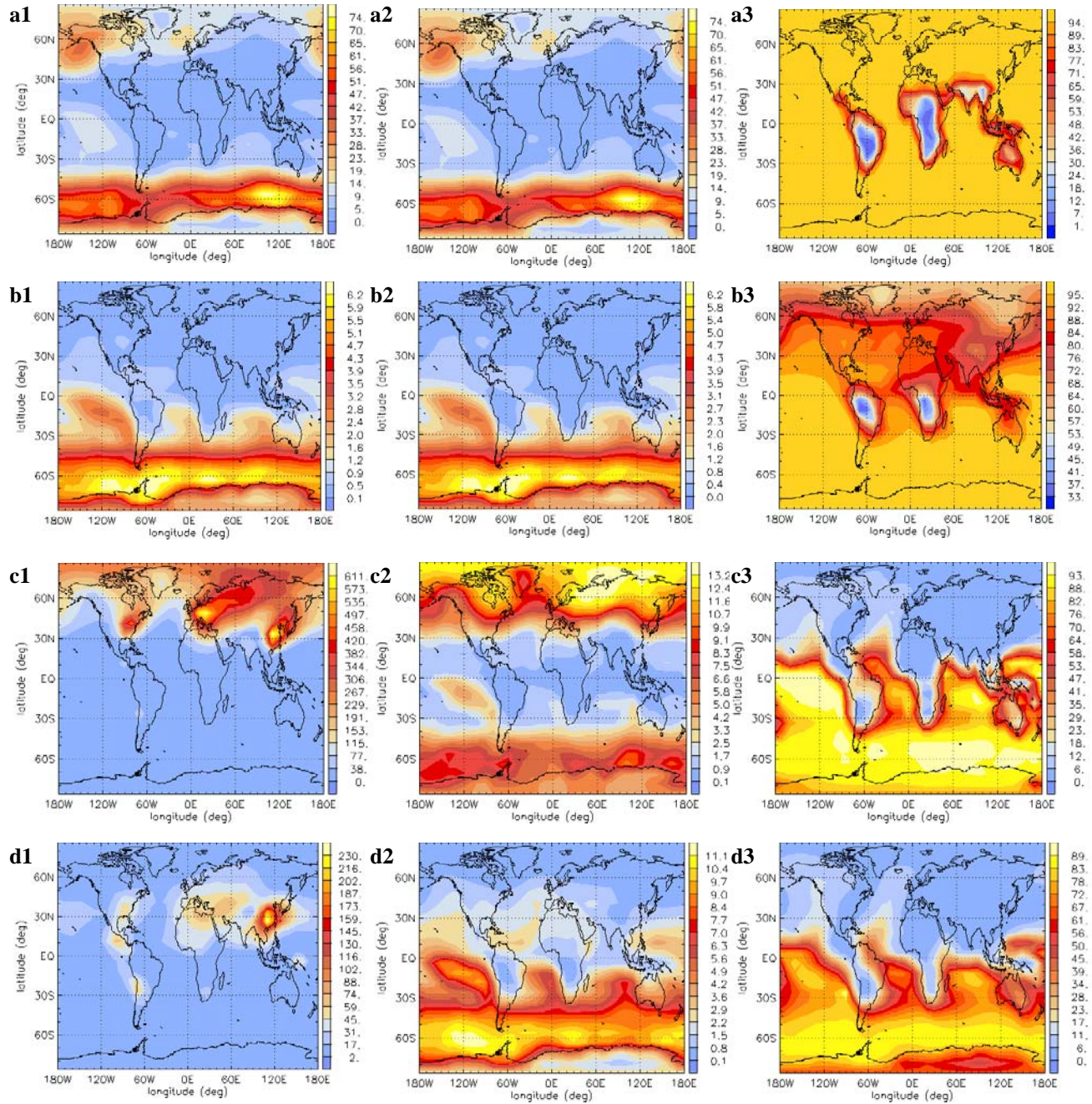


Figure 2: **a1, b1, c1, d1)** December-January-February mean column burdens ($\mu\text{mol m}^{-2}$) of DMS, MSA, SO₂ and nss SO₄⁻, respectively, resulting from both oceanic and terrestrial sources; **a2, b2, c2, d2)** those resulting from oceanic DMS emissions alone, and; **a3, b3, c3, d3)** the percentage of DJF averaged DMS, MSA, SO₂ and nss SO₄⁻ column burdens, respectively, that can be attributed to oceanic DMS emissions alone.

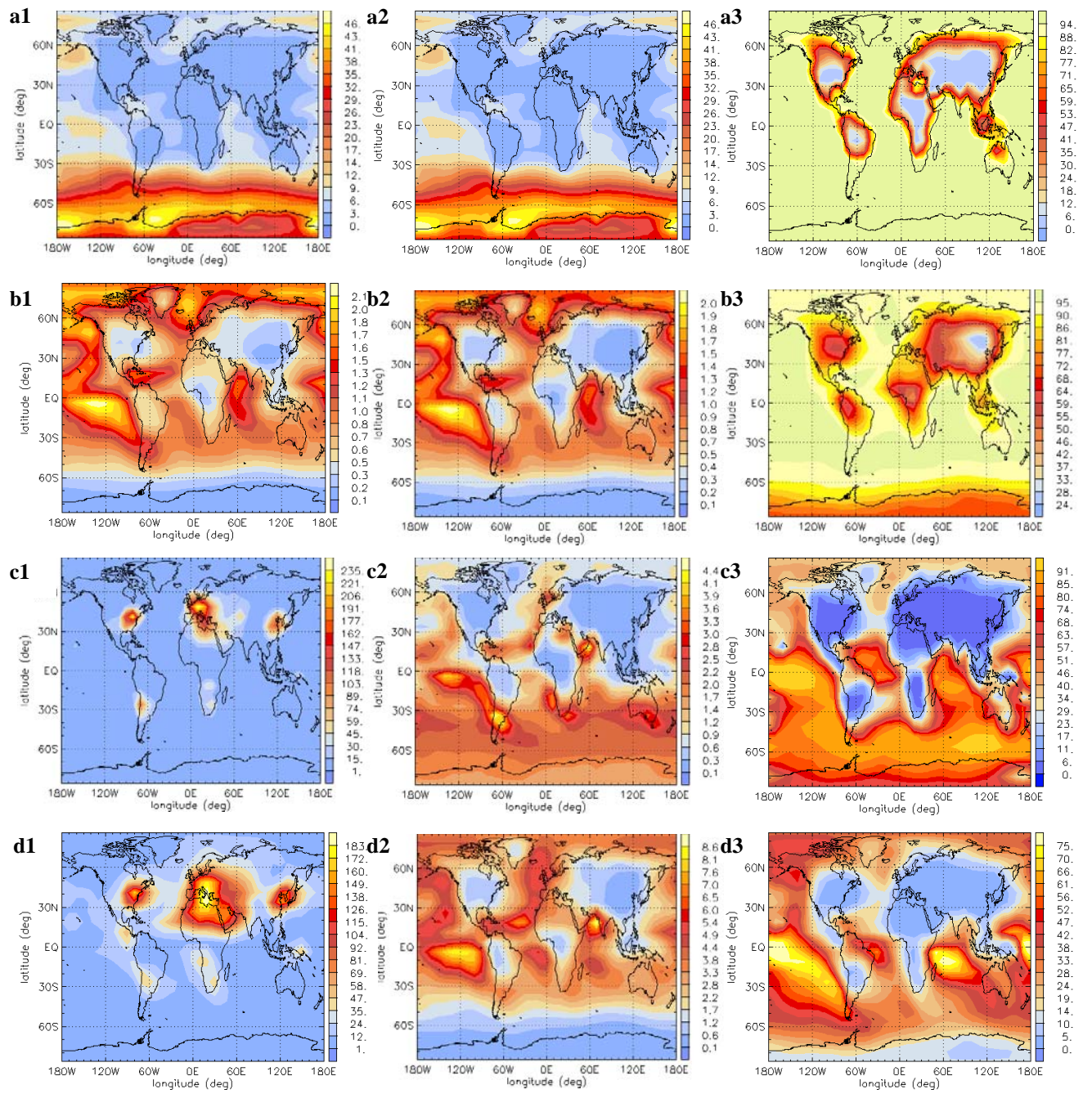


Figure 3: Same as Figure 2, but for the months of June-July-August.

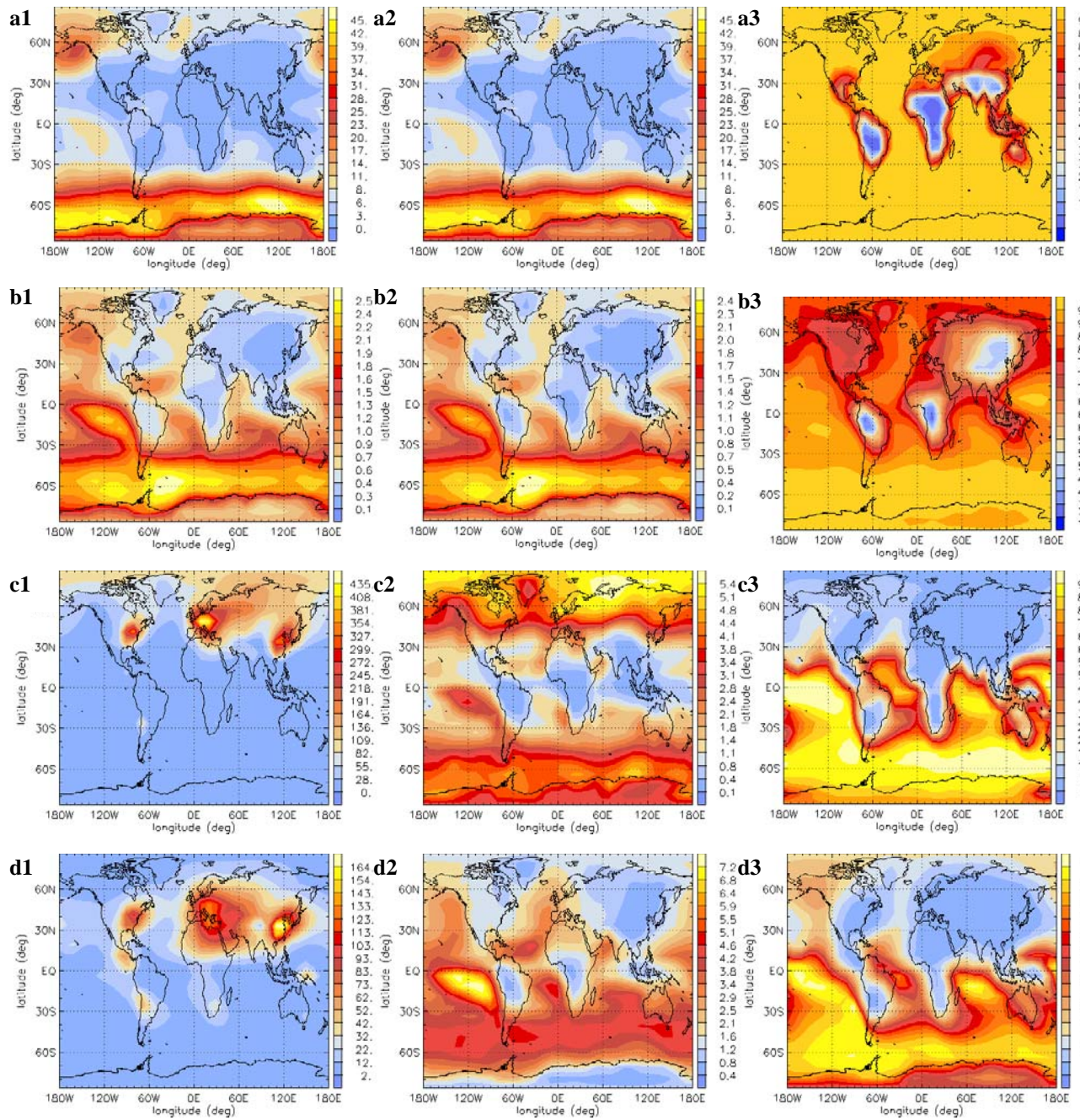


Figure 4: Same as Figure 2, but for an annually averaged period.

atmospheric DMS resulting from both oceanic and terrestrial sources (hereafter referred to as “all” sources) are shown in Figures 2a1, 3a1 and 4a1, respectively. The highest burdens (even during June–July–August, the Northern Hemispheric summer) occur in the Southern Hemisphere, specifically in a broad band above the Southern Ocean (also see Figures 5a1 and 6a1). This is, at first glance, surprising as the highest seawater DMS concentrations occur in the hemisphere that is experiencing summer and where phytoplankton occurrence and seawater DMS concentrations are also highest [Kettle *et al.*, 1999]. However, this effect may partly be explained through the different atmospheric oxidative capacities of the two hemispheres. The lifetime of DMS depends upon the atmospheric concentration of its two major oxidants: OH and NO₃, both of which are NO_x (nitrogen oxides = NO (nitrous oxide) + NO₂ (nitrogen dioxide)) dependent [Crutzen and Zimmermann, 1991; Thompson *et al.*, 1993; Davison *et al.*, 1996; Andreae and Crutzen, 1997].

OH is formed primarily as a result of photolysis of O₃ by solar ultraviolet radiation and the subsequent reaction of the photolysis product O(¹D) with water vapour [Crutzen and Zimmermann, 1991]. Tropospheric O₃ is in turn produced by the photochemical oxidation of NO_x and hydrocarbons, both of which have strong anthropogenic sources. The reaction of OH with many species also initiates a catalytic cycle which reforms OH. For example, the reaction of OH with carbon monoxide (CO) in the presence of oxygen produces hydroperoxyl radicals (HO₂) and carbon dioxide (CO₂). In turn, the HO₂ which is formed reacts with NO to reform OH and also produce NO₂. This NO₂ may in turn be photolysed in the presence of oxygen to form NO and O₃. O₃ is further photolysed, and in the presence of water vapour reforms OH.

Although the oxidant formation mechanisms operate in the same way all over the globe, the larger and more industrialised land masses of the Northern Hemisphere ensure an ample supply of OH and NO₃ to the Northern Hemispheric atmosphere, and therefore greater DMS removal. Even during the dark winter months around the North Pole, industrial emissions from the nearby continents ensure an abundant supply of NO₃ (verified by long-term measurements of aerosol nitrate (NO₃⁻) from a network of stations [Prospero *et al.*, 1995]), which continues to oxidise DMS in the absence of OH. OH production and abundance are sunlight driven and so it exists only

during daytime and is not available as an oxidant for the removal of DMS in the dark winter months at high latitudes. NO₃, on the other hand, has a nighttime abundance and a daytime scarcity due to its rapid photolysis [Atkinson, 1991 and Wayne *et al.*, 1991] and so is the major oxidant of DMS during dark periods. The less industrialised Southern Hemisphere (especially the remote area south of 50°S) has a limited supply of NO₃ for the removal of DMS during the long dark winter months of June–July–August (also verified by long-term measurements of aerosol nitrate on Antarctica [Savoie *et al.*, 1993]), resulting in an accumulation of DMS and an increase in its atmospheric burden.

Measurements of both seawater and atmospheric concentrations of DMS during a ship cruise along a transect through the Atlantic ocean by Burgermeister *et al.* [1990] led to the same conclusion. Although seawater DMS concentrations were measured to be higher in the N. Atlantic than in the S. Atlantic, these authors found that the mean atmospheric DMS concentration was higher above the S. Atlantic than above the N. Atlantic. They attributed this to a faster oxidation of DMS in the Northern Hemisphere.

Our findings of a high DMS burden above Antarctica throughout the year are also supported by field/model studies by Davis *et al.* [1998] during Project SCATE in the austral summer. These authors observed a very shallow marine boundary above the Palmer peninsula in which UV levels (and, therefore, OH production) are reduced. The consequently diminished oxidative removal of DMS resulted in an extended DMS lifetime of 7–9 days, which is relatively high for the summer period (elsewhere, the lifetime of DMS has been estimated to vary from approximately half a day in summer to about a week in winter [Gabric *et al.*, 1996]). If DMS was found to have such a long lifetime in summer when OH levels are at their highest, one can presume at least a similar, if not longer, lifetime of DMS above Antarctica during the long dark winter months when OH is absent and NO₃ is minimal.

Next to atmospheric chemistry, atmospheric dynamics and orography also play an important role in determining the magnitude of the DMS burden in a particular location within a hemisphere. In the Northern Hemisphere, a larger land surface area and orography perturb the atmospheric circulation encouraging the mixing of air masses and their chemical contents between the low-, mid- and high-

latitudes. This leads to the spatial dilution of DMS concentrations. On the other hand, the Southern Hemisphere has a greater oceanic surface area, with most of the land masses being concentrated in the low latitudes. Atmospheric perturbation and consequent meridional mixing between the low- and mid- and high-latitudes is, therefore, limited. The strongly zonal southern circumpolar flow results in the local elevation of the DMS burden in the mid- and high-latitudes.

In addition to differing oxidative capacities and orography, the Southern Hemisphere has a greater ocean surface area from which DMS is emitted when compared to the Northern Hemisphere. Furthermore, the sea-to-air transfer of gases has generally been found to be higher in rough and stormy seas [e.g. Watson *et al.*, 1991]. Frequent and rough storms which track along the high southern latitudes result in higher concentrations of DMS in the Southern Hemispheric atmosphere than in the Northern Hemispheric atmosphere. Burgermeister *et al.* [1990] measured relatively low atmospheric DMS concentrations over the N. Atlantic, where the mean DMS supersaturation in the water was a factor of 6 higher than that determined in the S. Atlantic on the same measurement campaign. They similarly attributed this to a diminished gas exchange between water and air, which could have been caused by the lower mean wind speeds simultaneously measured in the N. Atlantic. High atmospheric DMS concentrations measured in the English channel towards the end of the cruise by these authors were partly attributed to increased fog and subsequent decreased incident solar radiation which reduced the photochemical production of OH, a major DMS oxidant.

Comparisons of globally observed and modelled boundary layer concentrations are made in Table 2. The relatively coarse spatial resolution which we have selected for our model runs inhibits exact point-to-point correlation of the magnitude of modelled results with measurements. Nevertheless, the values are presented and comparisons in spatial and temporal trends are made. TM3 performs reasonably well in simulating atmospheric DMS concentrations over most regions, but overestimates concentrations above the Drake Passage and Weddell Sea off Antarctica as well as above the United Kingdom. Some underestimation is noted in the Eastern Mediterranean and Sargasso Sea. These differences

may be attributed to differences in the temporal scales of the measurements and the modelled concentrations. Most of the observed data are multi-year measurements (spanning even up to 11 years for MSA). The effects of meteorology (e.g. changes in wind speed and source direction) on concentrations recorded at a monitoring station and the location of hotspots are, therefore, smoothed out in these measurements. Our modelled concentrations are based on a 1-year record, which is inevitably strongly influenced by the specific meteorology of that year. Temporal trends are, in general, reasonably well reproduced by the model, with concentrations being higher in summer than in winter (e.g. in the Southern ocean [Curran *et al.*, 1998] and at Cape Grim [Ayers and Gillett, 2000]). Global spatial patterns of lower atmospheric DMS (and MSA) reproduced by TM3 are comparable to those modelled by Chin *et al.* [1996, 2000a] and Koch *et al.* [1999].

The global spatial distribution and magnitude of December-January-February, June-July-August and annually averaged column burdens of atmospheric DMS of oceanic origin (Figures 2a2, 3a2 and 4a2, respectively) are largely similar to those of DMS resulting from all sources (also see Figures 5a1 vs 5a2; 6a1 vs 6a2). The contribution of seawater DMS to the column burden of atmospheric DMS within the tropics is low relative to that in extratropical regions (Figures 5a3 and 6a2). This is due to the fact that terrestrial DMS emissions are highest in the warm and wet tropical areas, where they have a very small seasonal cycle, and where they overwhelm the oceanic source.

The globally averaged annual mean burden of DMS of oceanic origin is $11.9 \mu\text{mol m}^{-2}$ (98% of the total global DMS burden, Table 3). This huge contribution is not surprising since oceanic DMS emissions are globally the largest atmospheric DMS source. Spatially, the contribution of seawater DMS to the total column burden of DMS is greatest over all oceanic and polar regions in all seasons (Figures 2a3, 3a3 and 4a3). The lowest contribution occurs above continental regions, where terrestrial sources are more important and where oxidant levels are higher. The flux of DMS from continental sources increases exponentially with temperature [Bates *et al.*, 1992a]. This temperature dependence results in a significant seasonal cycle of atmospheric DMS burdens at continental high latitudes, but not within the tropics where temperatures are more stable.

Table 2: Observed versus modelled boundary layer concentrations of DMS and MSA resulting from all sources.

SITE	PERIOD	SURFACE CONCENTRATION ¹ (ppt)				REFERENCE ²	
		DMS		MSA			
		Observed	Modelled	Observed	Modelled		
Arctic:	Alert, Canada	'80 - '91	-	-	1.8	3.5	LJ1, LJ2, LB
	Barrow, Alaska	Feb - Apr '88	-	-	0.4 - 1.7	1.5	LJ1
		Mar - Apr '89	-	-	1.5	1.8	LJ1
	Dye, Greenland	Aug '88 - Jul '89	-	-	0.35	3.0	LJ1
	Greenland Summit	Jun - Jul '89	-	-	0.7	7.5	LJ1
		Jun - Aug '90	-	-	1.4	8	LJ1
N. & S. Atlantic:	N. Atlantic (open ocean)	Apr - May '84	75	80	-	-	AN1
	Along U.S. East Coast	Sep '85 - Sep '86	68.3	30	-	-	BE3
	Off U.S. East Coast	Sep '85 - Sep '86	33.3	20	-	-	BE3
		Aug - Sep '89	<DL - 150	20	-	-	JB, CS, AN2, GR
	Off and along U.S. East Coast	Sep '85 - Sep '86	-	-	7.9	1.3	BE3
	Sargasso Sea	Jun '84	178	40	-	-	AN1
	Gulf of Mexico	Oct '85	25	20	-	-	SC
	Miami	Jul '91 - Mar '93	-	-	10.3	1.5	PR
	Tropical S. Atlantic	Aug - Sep '89	9 - 104	70	-	-	JB, CS, AN2, GR
		Feb - Mar '91	50 - 300	50	-	-	AN3, AN4, SU
	Bahamas	Nov '83	94	140	-	-	AN1
		Jun '85	154	80	-	-	SC
	Barbados	Jul '91 - Mar '93	-	-	4.7	1.9	PR
	Bermuda	Jul '91 - Mar '93	-	-	8.5	1.9	PR
	Caribbean Transect	Feb - Mar '86	83	50	-	-	PR
Heimacy, Iceland	Jul '91 - Mar '93	-	-	8.7	4.1	PR	
Mace Head, Ireland	Jul '91 - Mar '93	-	-	13.6	4.8	PR	
United Kingdom	1988 - 1990	45	109	1.41	4.8	DH	
Tenerife	Jul '91 - Mar '93	-	-	0.94	2.5	PR	
Eastern Mediterranean (Greece)	May '97 - Oct '99	55	25	-	-	KM	
	Oct '96 - Sep '99	-	-	6.3	1.5	KM	
Atlantic Ocean Transects:	S. Atlantic	Mar - Apr '87	23.5	50	-	-	BU
	N. Atlantic	Mar - Apr '87	20	40	-	-	BU
	Iceland to Argentina (60°N-45°S)	Oct '96	29-396	1 - 240	-	-	SRI
	U.K. to Antarctica	Oct '92 - Jan '93	<DL - 549	1 - 400	0.4 - 85	1 - 48	DV

Table 2 (Continued)

Southern Ocean + Antarctic:							
Drake Passage, Bransfield & Gerlache Straits Weddell Sea S. Atlantic (68°S, 4°W) Palmer Mawson Marsh Cape Grim	Mar - Apr '86	96	410	6.2	10.6	BE1	
	Nov - Dec '90	147	390	-	-	SG	
	Nov - Dec '90	23	340	-	-	SG	
	Nov - Dec '90	671	510	-	-	SG	
	Apr '90 - May '91	-	-	11.5	15.7	SA3	
	Jan - Feb '94	6 - 595	85	3.3 - 146	55	BE4	
	Mar '87 - Dec '91	-	-	5.4	10.3	SA2, SA3	
	Jul '91 - Mar '93	-	-	4.9	10.3	PR	
	Apr '90 - Apr '91	-	-	7.1	12.7	SA3	
	Jan - Feb '84	128	25	-	-	ANI	
Southern Ocean, off Cape Grim	Nov '88 - May '96	12 - 235	10 - 140	0.47 - 50	2 - 30	AY1, GI, AG	
	Nov '88 - Mar '93	55	64	-	-	AY3	
	'76 - '91	-	-	4.1	10.6	AY2, GI	
	Dec '86	15 - 60	80	11	16	BE2	
	Nov - Dec '95	24 - 350	80	-	-	BR	
Macquarie Island	Dec '88 - Sep '91	-	-	<0.2 - 16.5	9	GI	
N. Pacific:							
	Midway Island	'81 - '87	-	-	7.1	5	SA1
		'81 - '82	-	-	7.1	5	SP
Equatorial Pacific:	Shemya Island	'81 - '86	-	-	22.8	7.2	SP, SA1
S. Pacific:	Fanning Island	Feb - Mar '91	352	200	10	5	HU
		July '82	124	290	-	-	ANI
		'81 - '86	-	-	10.3	4.8	SA1
		Apr '81 - Aug '82	-	-	10.6	4.8	SZ, SP
	American Samoa	Mar '83 - Aug '84	-	-	6.1	3.4	SZ, SP
		03/83 - 04/84, 01/90 - 04/92	-	-	5.4	3.4	SA4
		Jul '91 - Mar '93	-	-	5.9	3.4	PR
		'83 - '87	-	-	5.6	3.4	SA1
	Norfolk Island	'83 - '87	-	-	5.4	6.3	SA1
New Caledonia	'83 - '84	-	-	5.9	6.3	SP	
	'83 - '87	-	-	4.7	4.2	SA1	
	'83 - '84	-	-	5.9	4.2	SP	
Leigh, New Zealand	Dec '90 - Nov '92	5.9 - 350	50 - 150	-	-	WM	
	1991, 1992	-	-	11.5, 19	8.4	WM	

Table 2 (Continued)

Indian Ocean:		Amsterdam Island					
		'84, '87, '88, '89	23.5 - 376	30 - 300	-	-	NG
		'90-'99	182	179	-	-	SR2
		Jan '90-'99	570	800	-	-	PU, SR2
		Feb '90-'99	364	100	-	-	PU, SR2
		Mar '89-'99	214	200	-	-	PU, SR2
		Apr '89-'99	112	170	-	-	PU, SR2
		May '89-'99	85	90	-	-	PU, SR2
		Jun '89-'99	58	150	-	-	PU, SR2
		Jul '89-'99	38	70	-	-	PU, SR2
		Aug '89-'99	39	100	-	-	PU, SR2
		Sep '89-'99	65	50	-	-	PU, SR2
		Oct '89-'99	113	50	-	-	PU, SR2
		Nov '89-'99	164	190	-	-	PU, SR2
		Dec '89-'99	363	180	-	-	PU, SR2

¹ where a range is given the values correspond to a minimum and maximum. A single value represents a mean. <DL means below detection limit.

² AG = Ayers and Gillet [2000]; AN1 = Andrae *et al.* [1985]; AN2 = Andrae *et al.* [1993]; AN3 = Andrae *et al.* [1994]; AN4 = Andrae *et al.* [1995]; AY1 = Ayers *et al.* [1991]; AY2 = Ayers *et al.* [1986]; BE1 = Berresheim *et al.* [1987]; BE2 = Berresheim *et al.* [1990]; BE3 = Berresheim *et al.* [1991]; BE4 = Berresheim *et al.* [1998]; BR = De Bruyn *et al.* [1998]; BU = Burgermeister *et al.* [1990]; CS = Cooper and Saltzman [1993]; DH = Davison and Hewitt [1992]; DV = Davison *et al.* [1996]; GI = Gillett *et al.* [1993]; GR = Gregory *et al.* [1993]; HU = Huebert *et al.* [1993]; JB = Johnson and Bates [1993]; KM = Kouvarakis and Mihalopoulos [2002]; LB = Li and Barrie [1993]; LH = Li *et al.* [1993a]; LJ2 = Li *et al.* [1993b]; NG = Nguyen *et al.* [1992]; PR = Prospero *et al.* [1995]; PU = Putaud *et al.* [1992]; SAI = Savoie *et al.* [1989]; SA2 = Savoie *et al.* [1992]; SA3 = Savoie *et al.* [1993]; SA4 = Savoie *et al.* [1994]; SC = Saltzman and Cooper [1988]; SG = Staubes and Georgii [1993]; SP = Savoie and Prospero [1989]; SR1 = Sciare *et al.* [2000a]; SR2 = Sciare *et al.* [2000b]; SU = Suhre *et al.* [1995]; SZ = Saltzman *et al.* [1985]; WM = Wylie and de Mora [1996].

3.4.2 Methanesulphonate (MSA)

The spatial distribution of December-January-February and June-July-August mean column burdens of MSA resulting from all sources are shown in Figures 2b1 and 3b1, respectively. The highest column burdens occur in summer (December-January-February in the Southern Hemisphere, up to $6.2 \mu\text{mol m}^{-2}$ and June-July-August in the Northern Hemisphere, up to $2.1 \mu\text{mol m}^{-2}$). These modelled patterns are consistent with observations by Davison *et al.* [1996]. While the TM3 model performs generally well in reproducing observed MSA measurements at most stations, it seems to consistently overpredict these concentrations above Greenland by approximately a factor of 10 (see Table 2). Comparisons with results from other model studies reveal TM3 simulation of the surface spatial distribution of MSA to be in close agreement with patterns simulated by Koch *et al.* [1999] and Chin *et al.* [2000a].

The MSA spatial distribution pattern during December-January-February reflects a drawing in of air from the Southern Ocean (where the highest concentrations occur) to the S. Pacific, S. Atlantic and Indian oceans by southeast trade winds. The highest concentrations occur to the east of the oceans, and become less towards the west as most of the aerosol is lost through deposition in its long-range transportation (Figure 2b1). Air above these oceans has a descending motion, which suppresses precipitation and wet deposition. Removal of MSA is dominated by wet deposition [Benkovitz *et al.*, 1994] and so once this aerosol, and indeed nss SO_4^- and soluble gases such as SO_2 (Figures 4c2 and 4d2), are blown into these regions by trade winds, they are lost slowly and have a prolonged lifetime. On an annual scale, the highest annually averaged burdens of MSA resulting from all sources (up to $2.5 \mu\text{mol m}^{-2}$) occur in the Southern Hemisphere, specifically above the Southern Ocean and S. Pacific ocean (Figures 5b1, 4b1 and 6b1). This is attributed to the high DMS burden in these regions (see Figure 4a1). The high modelled burden of MSA above the Southern Ocean is in agreement with long-term measurements made in the Southern Hemisphere (see Table 2).

The global spatial distribution and magnitude of MSA column burdens resulting from DMS emissions of oceanic origin (Figures 2b2, 3b2 and 4b2, respectively) are largely identical to those of MSA resulting from all sources (also see Figures 5b1 vs 5b2;

6b1 vs 6b2). This is not surprising since atmospheric DMS oxidation is the only known source of MSA [Calhoun *et al.*, 1991; Huebert *et al.*, 1993; Legrand, 1997; Jefferson *et al.*, 1998]. Davison *et al.* [1996] similarly found a coincidence of DMS and MSA concentration trends in shipboard measurements made along a transect through the Atlantic ocean from the United Kingdom to Antarctica.

Differences in the DMS and MSA fields are noted around the polar regions (*e.g.* Figures 2a1 vs 2b1 and 2a2 vs 2b2). In these examples, DMS exhibits an elevated burden around the Arctic region (where it is winter) while the MSA burden is elevated only in the Southern Hemisphere (where it is summer). This difference is caused by season- and light-induced variations in oxidant availability. In the dark winter period in the Northern Hemisphere, there is hardly any conversion of DMS to MSA since OH availability is light limited. As discussed earlier, MSA is produced only through the reaction of DMS with the OH radical. The reaction of DMS with the nitrate radical produces only SO_2 as a product. Therefore, the $\text{DMS} + \text{NO}_3 \rightarrow \text{SO}_2$ oxidation pathway is dominant in the dark winter months around polar regions. This is evident in Figure 2c2, where SO_2 concentrations resulting from DMS oxidation are elevated around the Arctic region where DMS (but not MSA) burdens are also elevated.

The globally averaged annual mean burden of MSA of oceanic origin is $0.95 \mu\text{mol m}^{-2}$ (94% of the total global MSA burden, Table 3). This huge contribution is not surprising since oceanic DMS emissions are globally the largest MSA source. Figures 2b3, 3b3 and 4b3 show spatial distribution of the percentage of MSA that can be attributed to DMS emissions of oceanic origin. During December-January-February, the contribution of seawater DMS contributes to the total column burden of MSA is greatest in the Southern Hemisphere, where the atmospheric burden of its precursor DMS is also greatest. This contribution is lower over the Southern Hemispheric continental regions (where terrestrial sources are more important and oxidant levels are higher) and over the North Pole (where MSA advected from continental regions is also abundant). During June-July-August and on an annual scale, the contribution of seawater DMS to the total column burden of MSA is greatest in all oceanic areas of the globe and lowest over continental regions (Figures 3b3 and 4b3).

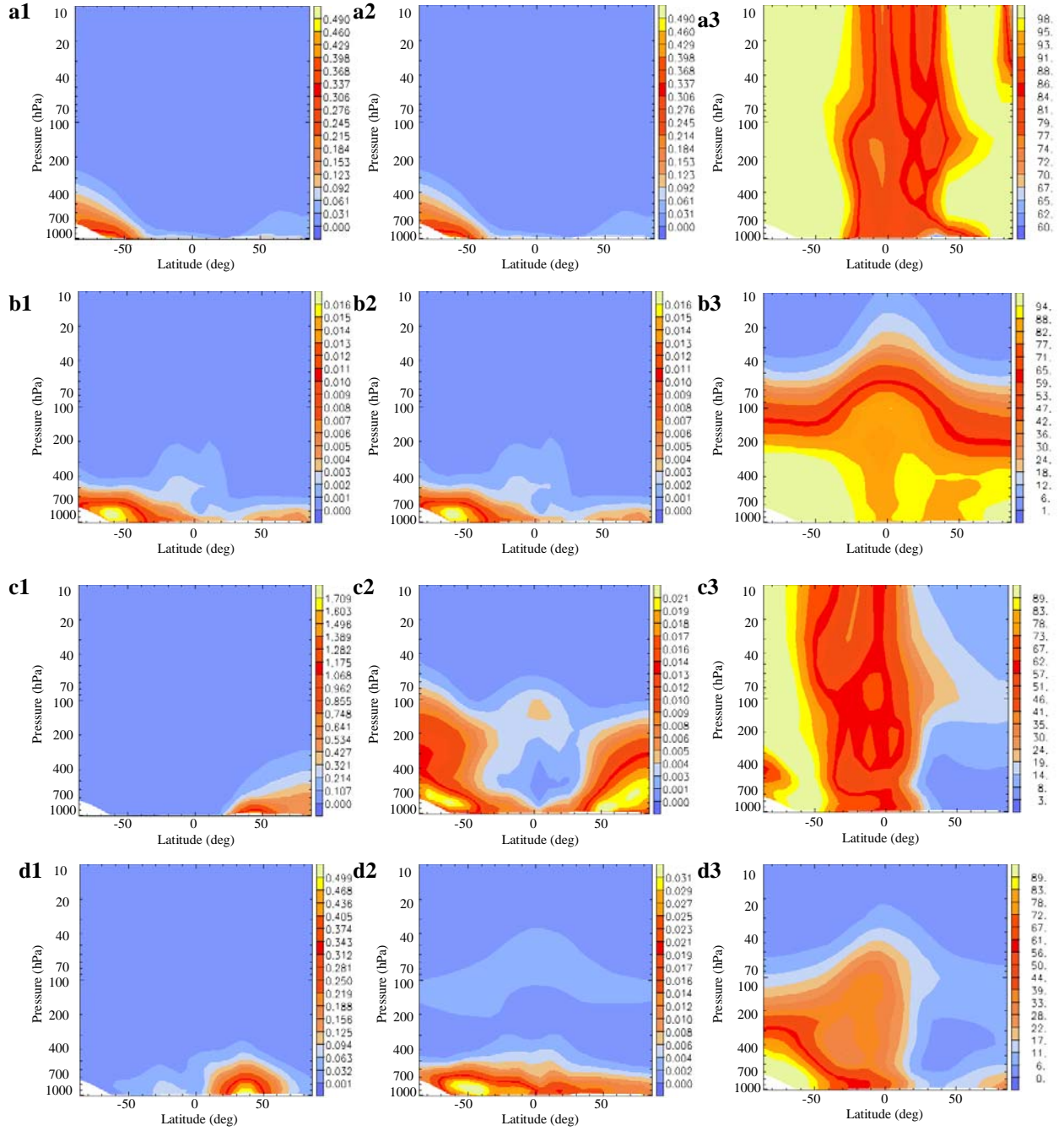


Figure 5: **a1, b1, c1, d1)** Annual zonal mean vertical distributions (ppb) of DMS, MSA, SO₂ and nss SO₄⁻, respectively, resulting from both oceanic and terrestrial sources; **a2, b2, c2, d2)** those resulting from oceanic DMS emissions alone, and; **a3, b3, c3, d3)** the percentage of annually averaged DMS, MSA, SO₂ and nss SO₄⁻ zonal mean vertical distributions, respectively, that can be attributed to oceanic DMS emissions alone.

3.4.3 Sulphur Dioxide (SO₂)

The spatial distribution of SO₂ column burdens resulting from all sources (Figures 2c1, 3c1 and 4c1, respectively) reflect the overwhelming year-long influence of anthropogenic sources in the Northern Hemisphere (also see Figure 5c1). The highest burdens (up to 500 $\mu\text{mol m}^{-2}$ in December-January-February; 150 $\mu\text{mol m}^{-2}$ in June-July-August; and 400 $\mu\text{mol m}^{-2}$ mean annually) are noted around the major source regions of China, eastern Europe and the eastern coast of the US and the polar areas to their north.

The global spatial distribution of SO₂ column burdens resulting from DMS emissions of oceanic origin (Figures 2c2, 3c2 and 4c2, respectively) differ from those resulting from all sources. During December-January-February and on an annual scale, the highest burdens occur in the midlatitude and polar regions of both hemispheres (also see Figures 5c2 and 6c2). The lowest burdens are noted within the tropics where the lifetime of SO₂ is shortened by relatively high concentrations of OH and H₂O₂ and convective transport to upper levels [Roelofs *et al.*, 1998]. During June-July-August, high SO₂ burdens are noted above the oligotrophic areas of the global ocean, where high atmospheric pressure and suppressed precipitation prevail. Suppressed precipitation results in a lower removal rate of SO₂ through its aqueous phase conversion to sulphate by H₂O₂ and O₃.

The globally averaged annual mean burden of SO₂ produced from oceanic DMS is 2.8 $\mu\text{mol m}^{-2}$ (32% of the total global SO₂ burden). On a hemispheric scale, the contribution of seawater DMS to the mean annual column burden of SO₂ resulting from all sources is greatest in the Southern Hemisphere where it is estimated at 61% (Table 3, Figures 5c3, 4c3 and 6c2). This contribution is less (22%) in the Northern Hemisphere where anthropogenic sources of SO₂ are dominant. During December-January-February and June-July-August the contribution of seawater DMS to the total column burden of SO₂ is also greater in the Southern Hemisphere than in the Northern Hemisphere (Figures 2c3 and 3c3). Even though June-July-August is winter in the Southern Hemisphere, elevated oceanic-derived SO₂ burdens occur over this area in this season due to a high DMS burden.

3.4.4 Non Sea Salt Sulphate (nss SO₄⁻)

The spatial distribution of nss SO₄⁻ column burdens resulting from all sources (Figures 2d1, 3d1 and 4d1, respectively) reflects the overwhelming year-long influence of anthropogenic sources in the Northern Hemisphere (also see Figure 5d1). This result is in agreement with longterm measurements of nss SO₄⁻ from a network of monitoring stations spread across the N. Atlantic ocean [Prospero *et al.*, 1995]. The highest burdens (up to 200 $\mu\text{mol m}^{-2}$ in December-January-February; 180 $\mu\text{mol m}^{-2}$ in June-July-August; and 150 $\mu\text{mol m}^{-2}$ mean annually) occur around the major source regions of China, eastern Europe and the eastern coast of the US. The spatial distribution pattern of nss SO₄⁻ simulated by TM3 is in agreement with that simulated by Koch *et al.* [1999] and Chin *et al.* [2000a].

The spatial distribution of the column burdens of nss SO₄⁻ resulting from oceanic DMS (Figures 2d2, 3d2 and 4d2, respectively) differs from that of nss SO₄⁻ resulting from all sources, but is similar to that of MSA aerosol, since both aerosols have common sinks and transport mechanisms. During December-January-February and on an annual scale, nss SO₄⁻ is picked up from the Southern Ocean (where the highest concentrations occur, also see Figures 5d2 and 6d2) by southeast trade winds and is brought to the atmosphere above the S. Pacific, S. Atlantic and Indian oceans. Some interhemispheric transfer of this nss SO₄⁻ is further evident and results in elevated concentrations in the tropical Northern Hemisphere. A consequence of this long range dispersion of this nss SO₄⁻ is the spread of the climate-modulating effects of DMS to areas of low plankton activity and DMS production. During June-July-August, elevated nss SO₄⁻ burdens are noted above the oligotrophic areas of the global ocean, where high atmospheric pressure and suppressed precipitation prevail. Suppressed precipitation results in reduced wet deposition - the main removal mechanism for SO₄⁻ [Langner and Rodhe, 1991; Huebert *et al.*, 1993; Benkovitz *et al.*, 1994; Lelieveld *et al.*, 1997; Chen *et al.*, 2000].

The globally averaged annual mean burden of nss SO₄⁻ of oceanic algal origin is 2.5 $\mu\text{mol m}^{-2}$ (18% of the total global nss SO₄⁻ burden). On a hemispheric scale, the contribution of seawater DMS to the mean annual column burden of nss SO₄⁻ is greatest in the

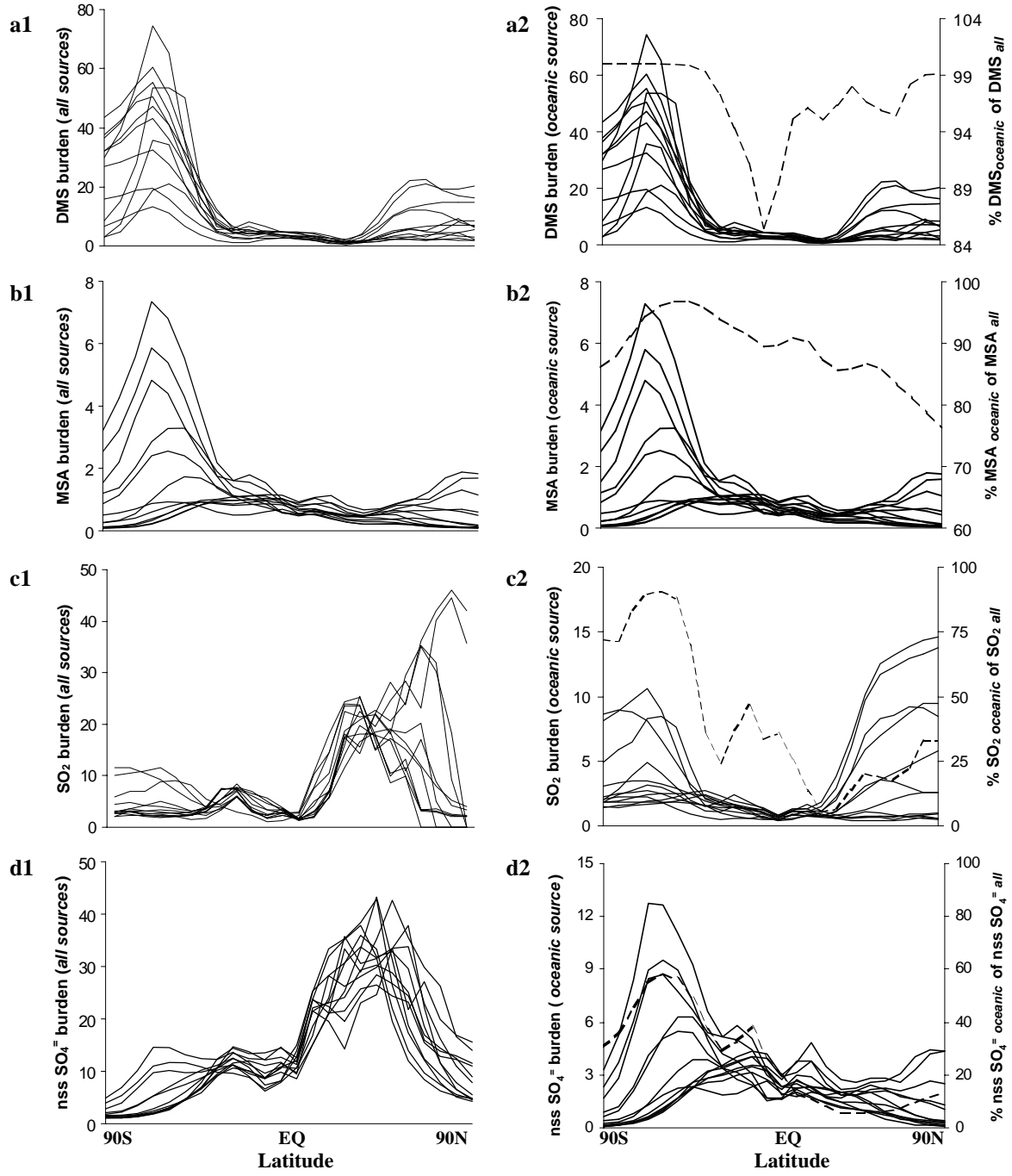


Figure 6: a1, b1, c1, d1) Zonal monthly means of the atmospheric DMS, MSA, SO_2 and nss $\text{SO}_4^=$ column burdens ($\mu\text{mol m}^{-2}$) respectively, resulting from both oceanic and terrestrial sources and, **a2, b2, c2, d2)** those resulting from oceanic sources only. The dashed line in a2, b2, c2 and d2 shows the percentage of zonal annually averaged DMS, MSA, SO_2 and nss $\text{SO}_4^=$ column burdens, respectively, that can be attributed to oceanic DMS emissions alone.

	ANNUAL MEAN COLUMN BURDENS ($\mu\text{mol m}^{-2}$)			ANNUAL MEAN SURFACE CONCENTRATIONS (ppt)		
	NH	SH	GLOBAL	NH	SH	GLOBAL
DMS oceanic	5.13	18.8	11.9	80	255	167
DMS total	5.24	18.9	12.1	85	260	172
% DMS oceanic of total	98	99	99	93	98	97
MSA oceanic	0.50	1.40	0.95	3.9	10.3	7.1
MSA total	0.56	1.45	1.01	4.1	10.4	7.3
% MSA oceanic of total	89	97	94	95	99	98
SO₂ oceanic	2.91	2.63	2.8	11	10	11
SO₂ total	13.3	4.3	8.8	668	32	350
% SO₂ oceanic of total	22	61	32	2	31	3
Nss SO₄⁻ oceanic	1.8	3.2	2.5	13	22	17
Nss SO₄⁻ total	20.9	7.4	14.2	222	41	131
% Nss SO₄⁻ oceanic of total	9	43	18	6	53	13

Table 3: Mean annual column burdens and surface (1009 hPa/ 35m) concentrations of DMS, MSA, SO₂ and nss SO₄⁻ resulting from both oceanic and terrestrial sources (“total”) and from oceanic DMS emissions alone (“oceanic”). The percentage contribution of seawater DMS to the total burdens and surface concentrations are also presented. This table was published in Gondwe *et al.* [2003b], as an erratum to a previous version which appeared in Gondwe *et al.* [2003a] (this chapter).

Southern Hemisphere, where it is estimated at 43% (Table 3). This contribution is only 9% in the Northern Hemisphere (also see Figures 4d3 and 6d2). During December-January-February and June-July-August the contribution of seawater DMS to the total column burden of nss SO₄⁻ is also greatest in the Southern Hemisphere (Figures 2d3 and 3d3). Even though June-July-August is winter in the Southern Hemisphere, elevated concentrations also occur over this area in this season due to a high burden of DMS (Figure 4a1). The high modelled burden of nss SO₄⁻ of oceanic DMS origin above the Southern Ocean is in agreement with long-term measurements made in the Southern Hemisphere [Davison *et al.*, 1996; Ayers and Gillett, 2000].

Agreement is, furthermore, found between our model results and isotopic measurements of the contribution of ocean-leaving DMS to nss SO₄⁻ at Mace Head in Ireland during summer by McArdle and Liss [1995] (~30%) [see Figure 3d3]. Similarly, our results are comparable to those obtained by Savoie *et al.* [2002] who conducted multiple regression analysis

of observations and estimated a 30% marine biogenic contribution to total nss SO₄⁻ above Bermuda; ~50% above Barbados; between 10-15% above Mace Head in Ireland and ~10% above Tenerife, just off the northwest African coast [see Figure 4d3].

3.4.5 Combined Results (DMS, MSA, SO₂ and nss SO₄⁻)

The contribution of seawater DMS to annually averaged column burdens and surface concentrations (1009 hPa / 35m) of DMS, MSA, SO₂ and nss SO₄⁻ is compared in Table 3. The spatial distribution of mean surface concentrations of DMS, MSA, SO₂ and nss SO₄⁻ resulting from all sources and from oceanic sources only, largely resemble those exhibited by their column burdens during all periods and are consequently not presented here or in a chapter of their own. We choose to discuss the burdens rather than the surface distributions as these are most relevant to climate considerations.

Globally averaged monthly mean burdens of

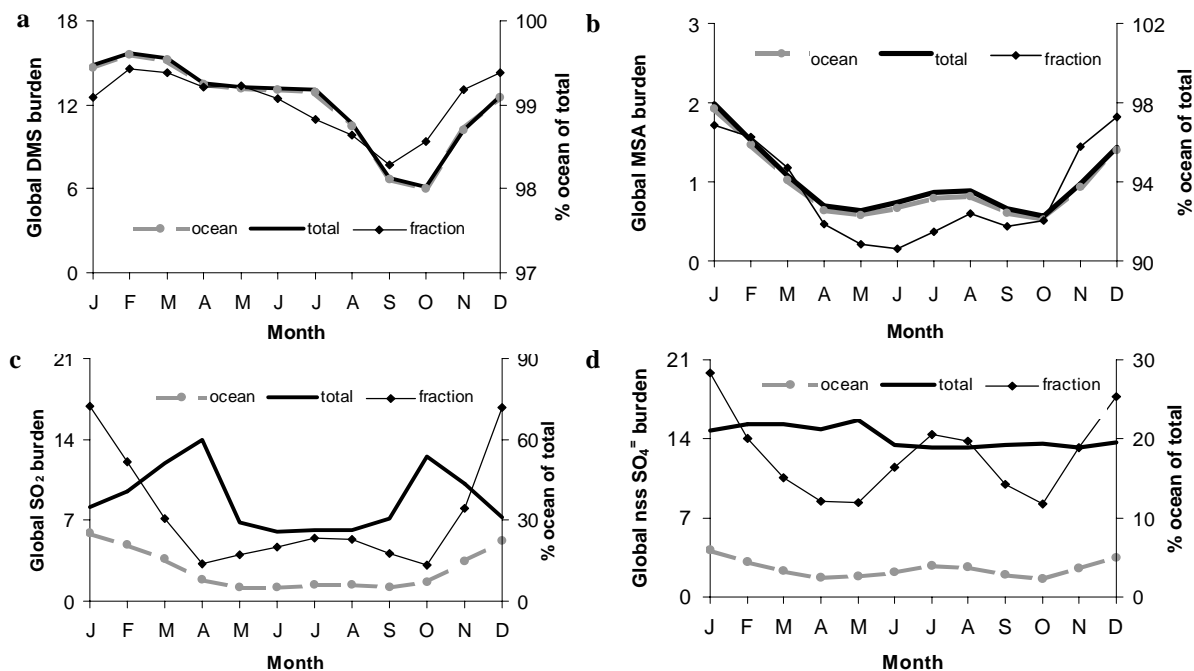


Figure 7: a, b, c, d) Global monthly mean column burdens of DMS, MSA, SO_2 and nss SO_4^{2-} , respectively ($\mu\text{mol m}^{-2}$). The global annual mean sulphur column burdens of oceanic algal origin are $11.9 \mu\text{mol m}^{-2}$ (99% of total global burden) for DMS; $0.95 \mu\text{mol m}^{-2}$ (94% of total global burden) for MSA; $2.8 \mu\text{mol m}^{-2}$ (32% of total global burden) for SO_2 ; and $2.5 \mu\text{mol m}^{-2}$ (18% of total global burden) for nss SO_4^{2-} . The second Y-axis shows the percentage of the global monthly averaged sulphur column burden that can be attributed to oceanic DMS emissions alone.

atmospheric DMS, MSA, SO_2 and nss SO_4^{2-} are presented in Figure 7. The temporal variability of the global mean of MSA closely follows that of its sole precursor atmospheric DMS, which in turn closely follows that of its major source seawater DMS. The highest global burdens of oceanic-derived DMS, MSA, SO_2 and nss SO_4^{2-} occur during the Southern Hemispheric summer months, when oceanic DMS emissions are greatest.

The vertical distribution of annually averaged DMS, MSA, SO_2 and nss SO_4^{2-} concentrations resulting from all sources and from oceanic sources only shows maximum concentrations in the boundary layer followed by the free troposphere (Figure 5 and Table 1). These patterns are in agreement with vertical profile measurements over the Atlantic, Pacific and Southern Oceans [e.g. Ferek *et al.*, 1986; Luria *et al.*, 1986, 1989; Andreae *et al.*, 1988, 1993; Berresheim *et al.*, 1990; Johnson and Bates, 1993; Cooper and

Saltzman, 1993; Li *et al.*, 1993a; Davison *et al.*, 1996; Davis *et al.*, 1999; Koch *et al.*, 1999; Barth *et al.*, 2000; Chin *et al.*, 2000b]. The highest concentrations resulting from all sources occur at latitudes south of 50°S for DMS and MSA (where the atmospheric DMS burden is greatest) and at latitudes between 30°N and 60°N (a region of overwhelmingly high industrial sulphur emissions; also see Table 1) for SO_2 and nss SO_4^{2-} .

Figures 5a3 and 5c3 show that the ratio of the gases DMS and SO_2 resulting from oceanic sources to those resulting from all sources is largely independent of altitude. MSA and nss SO_4^{2-} , however, show a decrease in this ratio with elevation, due to scavenging by precipitation.

While our study has improved upon several shortcomings in previous studies, the general accuracy of our model results is still constrained by a still-limited knowledge of DMS chemistry and kinetics;

shortcomings in some TM3 parameterisations and percentage yields selected for DMS oxidation products under varying temperatures; possible underestimation of DMS fluxes by the Liss and Merlivat method of flux determination (as much as a factor 2) [Bates *et al.*, 1994; Chin *et al.*, 1996; Turner *et al.*, 1996; Nightingale *et al.*, 2000]; and the paucity of data points in the Kettle *et al.* [1999] DMS database and shortcomings in their data interpolation procedure. We have also not considered two possibly important products of DMS oxidation by OH: dimethylsulphoxide (DMSO) and dimethylsulphone (DMSO₂) [Malin *et al.*, 1992; Lin and Chameides, 1993; Huebert *et al.*, 1993; Benkovitz *et al.*, 1994; Prospero *et al.*, 1995; Davis *et al.*, 1998; Jefferson *et al.*, 1998; Chen *et al.*, 2000; Arsene *et al.*, 2001]. While progress is being made in understanding their chemistry and kinetics, areas of major uncertainty still exist and critical information that would strengthen model parameterisations is missing.

3.5 Conclusions

Marine phytoplankton make an important contribution to the global sulphur cycle. Global three-dimensional chemical transport modelling shows that ocean-leaving DMS significantly contributes to the global annually averaged column burdens (from the surface to the lower stratosphere) of DMS (11.9 $\mu\text{mol m}^{-2}$, 98% of total global burden), MSA (0.95 $\mu\text{mol m}^{-2}$, 94% of total global burden), SO₂ (2.8 $\mu\text{mol m}^{-2}$, 32% of total global burden) and nss SO₄⁻ (2.5 $\mu\text{mol m}^{-2}$, 18% of total global burden). On a hemispheric scale, the mean surface seawater DMS concentration between the Northern and Southern Hemisphere is not significantly different. However, the contribution of seawater DMS to the mean annual column burden of nss SO₄⁻ (a climate-relevant aerosol) is greatest in the relatively pristine Southern Hemisphere, where it is estimated at 43%. This contribution is only 9% in the Northern Hemisphere, where anthropogenic sulphur sources are overwhelming. The huge contributions of oceanic DMS to the total atmospheric DMS and MSA burdens is not surprising since oceanic DMS emissions are globally the largest atmospheric DMS and MSA source. The global scope of our study has allowed identification of regions receiving the greatest marine algal-derived input of atmospheric sulphur components in the present day climate scenario.

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